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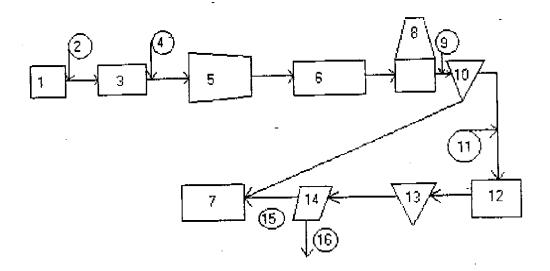
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(54) Improved procedure for treatment of pig manure and fertiliser product thereby obtained

(\$7) The present invention relates to improvements to a biological procedure for the treatment of pig manure, in which a much better degradation of liquid residues with a high contaminating load and/or high toxicity

is achieved, especially in reference to the elimination of ammonium nitrogen and total Kjeldahl nitrogen (TKN) present in the pig manure. The invention also relates to a new product resulting from the treatment process, of use in the agricultural sector as fertiliser.

Fig. 1



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Description

OBJECT OF THE INVENTION

[0001] The present invention relates to improvements to a biological procedure for the treatment of pig manure, in which a much better degradation of liquid residues with a high contaminating load and/or high toxicity, especially in reference to the elimination of ammonium nitrogen and total Kjeldahl nitrogen (TKN) present in the pig manure. The invention also relates to a new product resulting from the treatment process, of use in the agricultural sector as fertiliser.

1.

BACKGROUND OF THE INVENTION

[0002] The present patent relates to improvements to a biological procedure for the degradation of liquid residues, in particular pig manure. Said biological procedure is the object of the patents P9800763 and WO 97/47561 by the same applicant as the present application. In said patents a procedure is disclosed comprising distinct stages: an initial physical-chemical treatment, an anaerobic-aerobic mixed biological treatment, with different processes, and finally a conventional physical-chemical treatment.

[0003] The improved procedure of the present patent is based on a chemical reaction, known for its harmful nature in water piping, but which has never been applied to the treatment of pig manure, The reaction allows elimination of ammonium nitrogen and the total Kjeldahl nitrogen, thus tackling the problem of nitrogen removal in the treatment process.

[0004] Furthermore, another improvement with respect to the aforementioned patents, and with respect to the State of the Art, consists of obtaining a novel final product at the end of the procedure, rich in humic and fulvic acid, which may be used as liquid fertiliser. In the State of the Art, the humic and fulvic acid added to fertiliser are obtained by the extraction from organic material, which may be either compost or peat. In the novel procedure herein disclosed, treated pig manure is used as the source of these compounds for the production of a lertiliser for agricultural use.

SUMMARY OF THE INVENTION

[0005] To combine the application of the novel chemical reaction described above with the production of the novel fertiliser rich in humic and fulvic acid the following improvement in the treatment procedure has been developed.

[0006] To apply the procedure, prior to the application of the first improvement the virgin pig manure should be submitted to a sterilisation process the reactor. In this sterilisation process the mass of manure is heated, either within the reactor itself or into a smaller reactor prior to centrifugation. This prior sterilisation process or di-

gestion process allows the total Kjeldahl nitrogen to be converted into the form of ammonium nitrogen.

[0007] The first improvement in the procedure consists of eliminating the nitrogen content, now in ammonium nitrogen form, from the sterilised mass, by chemical precipitation, more specifically using the reaction to form "struvite" (magnesium ammonium phosphate), a reaction which allows almost all ammonia to be eliminated from the pig manure.

[0008] The reaction is effected by introducing specific reagents, namely magnesium and phosphate salts, into a strongly stirred reactor containing the sterilised pig manure at 70° C. Under these conditions the "struvite" (magnesium ammonium phosphate) formed precipitates out. The "struvite" reaction proceeds spontaneously, but as the molar quantities of reagent are not exactly balanced the reaction is partial. After the reaction has reached completion, a flocculating agent is added and the precipitated salts and solid and flouid fractions of the sterilised manure separated by centrifugation. The solid fraction, rich in nitrogen and phosphorus containing compounds is then discarded. This process leads to almost complete elimination of total Kjeldahl nitrogen (TKN).

[0009] The remaining liquid is then subsequently passed on for further treatment in a biological reactor (see patents P9800763 and WO 97/47561) to obtain a product consisting of water and nutrients. According to the prior art the semi-treated residual water is then released directly into the environment, although the semi-treated water may be harmful for the environment. The complete elimination of non-biodegradable compounds from a product is obligatory before it is released into the environment.

[0010] In the procedure of the present invention the semi-treated product is submitted to a further novel procedure in order to obtain a novel product which can be used for agricultural purposes. The procedure consists of heating the semi-treated liquid to effect partial evaporation thereof. After which a process of coagulation in the concentrate is induced by the addition of metallic salts and adjusting the pH to acidic values. The solid and liquid fractions are separated and the liquid fraction adjusted to a basic pH by the addition of a metal hydroxide salt, for example CaOH. The liquid is then passed through a membrane with a 5000-Dalton cut-off, which does not permit the passage of humle and fulvic acid. The resulting liquid concentrate is rich in humic and fulvic acid and is mixed with the solid precipitate from the earlier stage. The mixture is then adjusted to alkaline pH's to give the final product, which can be used in the agricultural sector as a fertiliser. The liquid that passes through the membrane can be released directly into the environment.

DESCRIPTION OF THE FIGURES

[0011] To facilitate a better understanding of the ideas

expressed above, the elements of the invention are described with reference to the illustrative figure accompanying this specification. The figure is purely for illustrative purposes and is non-limiting.

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[0012] Figure 1 shows a schematic block diagram representing an embodiment of the invention according to the procedure of the present invention.

DESCRIPTION OF A PREFERRED EMBODIMENT OF THE INVENTION

[0013] The process consists of treating liquid pig manure with the object of purifying it in order to reduce its contaminating effects and to obtain novel products. The untreated pig manure is subjecting to an initial cleansing. process in which the manure is heated to 70° C. During this homogenisation process (1) the Kjeldahl nitrogen content is converted to ammonium nitrogen. The plg manure then passes to a strongly stirred reactor (2) where magnesium and phosphorus salts are added. It then passes to a chamber (3) where the reaction to form "struvite" takes place spontaneously, leading to the elimination of 98% of the ammonium nitrogen in the mixture (virtually all the Kjeldahl nitrogen compounds in the initial untreated manure have been converted to the ammonium form during the cleansing process (1), thus effecting the almost complete elimination of nitrogen from the manure). After 15 minutes in the reaction chamber (3) a suitable organic flocculating agent is added (4) and the mixture submitted to centrifugation (5) to produce a solid and liquid fraction. The solid fraction, rich in nitrogen and phosphorus compounds, is composed of the precipitated "struvite" and the remaining solid material. This solid fraction is discarded. The liquid fraction, lean in nitrogen and phosphorus compounds, is introduced: into a biological reactor (6) where the biological purification process of the liquid part of the pig manure will continue.

[0014] Once the soluble fraction of the pig manure has passed through the biological reactor (6) semi-purified water is obtained containing nutrients, mainly humic and fulvic acids. The semi-purified water is now heated (the heat source preferably being derived from a co-generation process, for example, a process which simultaneously produces heat and electricity) to concentrate it by means of partial evaporation (8). The next step is a coagulation process whereby metallic salts and acids are added (9) to adjust the semi-purified water to an acidic pH, lying between 1 and 6. The precipitated fraction is separated by decantation (10). The remaining liquid fraction or supernatant is adjusted to a basic pH of between 7 and 12 by addition of CaOH (11) in a suitable reactor (12) before a further decantation step (13) and filtration through a Dalton membrane with a 5000 Dalton cut-off (14) to give a concentrated fraction and a liquid that may be released directly to the environment (15). The concentrated fraction is combined with the solid fraction from the previous precipitation step (10) and the

pH of the resulting mixture adjusted to a basic pH (greater than 7). The resulting mixture (7) is rich in humic and fulvic acid and may be used as a liquid fertiliser by the agricultural sector.

[0015] The procedure of the invention presents considerable advantages. The use of co-generation to produce the heat necessary for the evaporation step (8) reduces the energy costs of the process. There is a reduction in the quantity of contaminants produced by the process, allowing direct release into the environment and the liquid fertiliser is a novel product which has never before been attained from a manure treatment process.

Claims

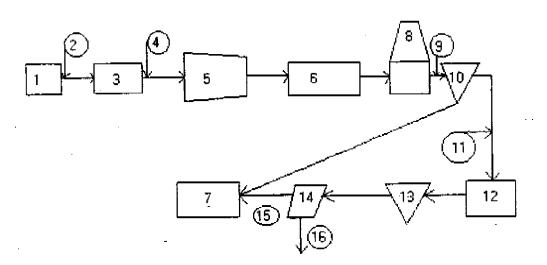
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- An improvement to a procedure for treatment of pig manure, said procedure pertaining to physical and chemical treatment of said pig manure followed by a biological treatment, characterised in that it comprises the additional steps of;
 - i) sterilisation (1) of the pig manure in its virgin state by heating said mass, converting the total Kjeldahl nitrogen into ammonium nitrogen passing said sterilised mass to a vigorously stirred reactor (2); and
 - ii) adding magnesium and phosphate salts (3) to induce rapid chemical precipitation of the ammonium nitrogen present in the sterilised-pig manure through the chemical precipitation of magnesium ammonium phosphate ("struvite") and, after the addition of a suitable organic floculant (4), centrifuging the resulting mixture (5) to separate the "struvite" and other solid material from the liquid fraction.
- A procedure according to claim 1, characterised because said liquid fraction is submitted to further treatment comprising; treating said liquid fraction in a biological reactor (6), partially evaporating the liquid (8) from said biological treatment, adding acid and metal salts (9) to induce precipitation, separat-45 ing the precipitate from the liquid fraction (10), adding a metal hydroxide (11) to bring the pH of said liquid fraction to a basic pH, passing said liquid fraction through a membrane with a 5000 Dalton cut-off (14) to produce a concentrate, mixing said concentrate with said precipitate (10), and adjusting the pH of the mixture to alkaline values to yield a high quality novel liquid fertiliser (7) of use in the agricultural sector.
- A liquid fertiliser obtained according to the previous claims, rich in fulvio and humic acid.

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Fig. 1



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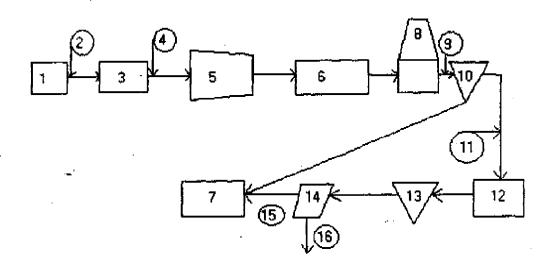
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Fig. 1



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EUROPEAN SEARCH REPORT

Application Number EP 00 50 0047

ategory	Citation of document with indi- of relevant passag	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)	
(EP 0 564 298 A (NGK 6 October 1993 (1993-	1	C05F3/00	
<i>(</i>	* the whole document	•	3	
Y	FR 2 686 814 A (ASS) 6 August 1993 (1993-1 * page 7, line 5 *	VALORIS DEJECT ANIMA) 08-06)	1	
Y	DATABASE WPI Section Ch, Week 1999 Derwent Publications Class CO4, AN 1995-1 XP002206969 & CN 1 083 461 A (LI) 9 March 1994 (1994-0) * abstract *	Ltd., London, GB; 79783 ANG Z).	3	
Y	EP 0 576 389 A (DREW: 29 December 1993 (199 * page 2, column 2 *		1	TECHNICAL PIELDS
A	US 5 531 907 A (WILL 2 July 1996 (1996-07 * page 11, column 2	1,2	COSF COSG COSB	
A	DE 44 44 032 C (KUEH 2 May 1996 (1996-05- * page 2, column 2 * * page 3, column 4 * * claim 1 *	1,2		
A	EP 0 701 983 A (CERE 20 March 1996 (1996- + the whole document	1,2		
A	US 5 593 590 A (STEY 14 January 1997 (199 * page 7, column 4 *	1,2		
		-/		
	The present search report has be			
	Place of search	Date of completion of the veterch		Examiner
X : par Y : par doc A : teo	MUNICH CATEGORY OF CITED DOCUMENTS It cutanty relevant if taken atons It cutanty relevant if combined with anothe sument of the same category hectogloal background written disclosure	L : document ched	ple underlying the ocument, but pub- late in the application for other reasons	llahed on, or 1

EP 1 041 058 A3



EUROPEAN SEARCH REPORT

Application Number EP 00 50 0047

	DOCUMENTS CONSIDERED			
tegory	Citation of document with indication of relevant passages	, where appropriate,	Flelevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
	WO 93 15026 A (CHEMRING 5 August 1993 (1993-08-0 * the whole document *	GROUP PLC) 5)	1,2	
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				TECHNICAL PIELDS
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	The present search report has been do	awn up for all claims Date of completion of the sex		Examine:
	Place of search MUNICH	22 July 2002		damli, S
X : pe Y : pe do	CATEGORY OF CITED DOCUMENTS who larry relevant it taken alone intollarly relevant if combined with another current of the same category chancegoal background	T : theory or E : earlier pa effer the f D : document L : document	principle underlying the tent document, but publishing date t cited in the application cited for other reasons	invention Ished on, or

. EP 1 041 058 A3

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 00 50 0047

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-07-2002

FR 26	564298	A	06-10-1993	JP JP JP JP JP JP	2659895 5345200 2083436 6071296 8000238 6071297 7115036	A C A B	23-08-1996 15-03-1994 10-01-1996
FR 26		•		JP JP JP JP JP	5345200 2083436 6071296 8000238 6071297	A C A B	27-12-1993 23-08-1996 15-03-1994 10-01-1996
CN 10			, ·	JP JP JP JP JP	2083436 6071296 8000238 6071297	C A B	23-08-1996 15-03-1994 10-01-1996
CN 10	. •			JP JP JP JP	6071296 8000238 6071297	A B	15-03-1994 10-01-1996
CN 10	. •			JP JP JP	8000238 6071297	В	10-01-1996
CN 10	. •			JP JP	6071297		
CN 10	. •			JP		^	15-03-1994
CN 10	. •				\ T T 3020	D	13-12-1995
CN 10				UI .	6099199		12-04-1994
CN 10				JР	7075717		16-08-1995
CN 10				DE	69319270		30-07-1998
CN 10				DE	69319270		03-12-1998
CN 10				EP	0564298		06-10-1993
CN 10				Ū\$	5360546		01-11-1994
CN 10					3300340		OT-11-1334
	686814 	A	06-08-1993	FR	2686814	A1	06-08-1993
EP O!	083461	A	09-03-1994	NONE			
	576389	Α.	29-12-1993	DE	4220947	Al	01-04-1993
				AT	144239		15-11-1996
				DΕ	59304165	D1	21-11-1996
			•	EΡ	0576389	A2	2 9- 12-1 9 93
US 59	5319 07	Α	02-07-1996	GB	2284205	А ,В	31-05-1995
DE 44	444032	С	02-05-1996	DE	4444032	CI	02-05-1996
EP 07	701983	A	20-03-1996	NL.	9401495	Α	01-04-1996
				CÃ	2158326		16-03-1996
				ĒΡ	0701983		20-03-1996
				ÑĹ	1001197	C2	12-09-1996
				NL	1001197		11-07-1996
				WC	9609269		28-03-1996
		-		ÜS	5993503		30-11-1999
is si	5 9 3590	A	14-01-1997	AT	137727	T	15-05-1996
	~~~~~ <del>*</del>	••	4. ~~ 400	CA	2104791		28-08-1992
				DÉ	59206247		13-06-1996
				WO	9215540		17-09-1992
				ËP	0573478		15-12-1993
	<b>-</b> '			ËS	2089502		01-10-1996
⊔∩ 0′			05-08-1993	AT	171697	 T	15-10-1998
	A LOUZD	• •	00 00 1330	AU			
	315026				00//31/	DZ.	Z4-D8-1445
	312050			AU	662207 3457193		24-08-1995 01-09-1993

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

## EP 1 041 058 A3

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 00 50 0047

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-07-2002

Patent docume cited in search re	ent eport	Publication date		Patent family member(s)	Publication date
WO 9315026	A		CZ DE DE EP FI WO GB JP NO RO SK	9401832 A3 69321343 D1 69321343 T2 0625961 A1 943555 A 9315026 A1 2277514 A ,B 7503178 T 942809 A 246914 A 114444 B1 90494 A3	15-02-1995 05-11-1998 20-05-1999 30-11-1994 30-09-1994 05-08-1993 02-11-1994 06-04-1995 28-07-1994 26-07-1995 30-04-1999 12-04-1995
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